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Identification and Distribution of Palygorskite in a Petrocalcic Paleargid

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ABSTRACT: *Palygorskite is a chain lattice phyllosilicate typically found in arid zone soils containing a calcic or petrocalcic horizon. Its presence was verified in a Petrocalcic Paleargid in the central desert of Baja California using several diagnostic techniques. X-ray diffraction of the clay and medium silt fractions of each horizon showed characteristic palygorskite peaks at approximately 10.4, 6.4, 3.6 and 3.2°A. Heating processes decreased the intensity of the 10.4°A peak and resulted in new peaks at 9.3 and 4.7°A in the Ckq horizon. Peaks in the clay fraction became broader and less intense, indicating lower concentration and poor crystallinity of palygorskite with decreasing depth. Thermal and infrared spectroscopic analyses corroborated XRD data. TGA weight losses occured at 50-150, 175-225 and 375-535°C, corresponding to loss of hygroscopic water, loss of zeolitic water and dehydroxylation, respectively. Decomposition weight loss was not seen at the characteristic high temperature (690-770°C). Additionally, IR absorbance bands were characteristic of palygorskite, occurring at 3620, 3580, 3530, 3415, 3290, 1660, 1180, 1030, 1000 and 930* cm^{-1}. *Finally, the TEM analysis revealed presence of acicular particles, increasing in abundance with depth, which were morphologically identical to palygorskite. Thus, the palygorskite was identified in the clay and medium silt fractions of the soil, showing its concentration and the degree of crystallinity with increased depth.*

INTRODUCTION

Palygorskite is a chain lattice phyllosilicate currently intriguing mineralogists because it is being increasingly found throughout the world in arid zone soils which contain a calcic or petrocalcic horizon. In the U. S., occurrences have been reported in the High Plains of Texas and New Mexico (McLean et al., 1972; McGrath and Hawley, 1987).

Palygorskite differs from other layer silicates with respect to its octahedral sheets, which are not continuous. Inversion of SiO_4 tetrahedra form an open framework of channels that run parallel with the edges of octahedral ribbons and the length of the fiber axis. Each ribbon is joined at the corners with virtually straight Si-O-Si bonds. There are five octahedral sites per structural unit in palygorskite. A high ratio of aluminum and a significant amount of vacancies cause it to tend toward dioctahedral character. Besides surface adsorbed water, it has unbound (zeolitic) water within its channels, water coordinated to the edge octahedral cations, and OH^- groups at centers of ribbons. The dimensions of palygorskite display typical width (100-300°A), thickness 50-100°A) and length (0.2-2μm) (Rausell-Colom and Serratosa, 1987).

Identification of palygorskite was made, using the standard diagnostic techniques which include X-ray diffraction, thermogravimetric analysis (TGA), infrared spectroscopy and electron microscopy. Wilson (1987), and Zelazny and Calhoun (1977) have extensively discussed criteria for identification of palygroskite using these methods.

The soil mineralogy of the Baja peninsula has to date received little attention. It was, therefore, of special interest to note the presence of palygorskite here within a Petrocalcic Paleargid. The objective of this paper is to describe how palygorskite was identified and its distribution observed throughout the soil profile.

MATERIALS AND METHODS

The study area was located on a mesa near San Agustin. The site is within a small area of post batholithic Miocene rhyolite, and is surrounded by large expanses of post batholithic Miocene fluvial sedimentary deposits and also pre-batholithic undifferentiated volcanic rock. Climte is Mediterranean, characterized by cool winters and warm, dry summers. Average annual rainfall is 110 mm. Native desert vegetation is present.

The soil is a fine loamy micaceous thermic Petrocalcic Paleargid. An abbreviated pedon description plus chemical and physical data are provided in Tables 1-3.

TABLE 1. TYPICAL PEDON DESCRIPTION OF RHYOLITE CENTRAL DESERT OF BAJA

Horizon	Depth (cm)	Color	Texture	Structure	Carbonates	Boundary
A1	0-2	7.5YR4/4 7.5YR4/4	Si 1	2f.mpl	em	as
ABtk	7-8	7.5YR5/4 7.5YR5/3	Siccl	2vf.f	es.flsm	aw
Btk1	8-18	5YR5/6 7.5YR4/6	Si Cl	3fsbk	ev.flsm	aw
Btk2	18-32	5YR4/4 5YR3/4	Si C	2cpr- 3Cpl	ev.flwm.sf	aw (rock) ag (carbonates)
Cl	32-36	7.5YR8/2 7.5YR7/2	Si Cl	1vf.sbk	ev	ab
Ckg	36-61	Concrete-like material containing andesite rock fragments. Appears to be in gross slabs or layers. Soil was sampled from between such slabs.				

TABLE 2. PHYSICAL ANALYSIS OF RHOLITE SOIL IN THE CENTRAL DESERT OF BAJA

S. #	Horizon	Depth (cm)	Gravel[1] Weight %	VCS	CS	MS	FS	VFS	TS	Silt[3]	Clay[4]	pH[5]	CaCo equiv.
				Sand[2]									
				Weight %									
1	A1	0-2	25	1.8	1.7	3.6	15.6	11.7	34.4	49.2	16.4	7.79	2.2
2	Abtk	2-8	14	0.8	1.5	3.1	12.5	9.5	27.4	52.3	20.3	7.82	2.7
	Btk1	8-18	8	0.8	1.1	2.7	9.7	7.2	21.5	47.8	30.6	7.50	4.2
3	Btk2	18-32	1	0.4	0.6	1.7	7.2	7.0	16.9	43.5	39.6	7.63	5.5
4	Ck	32-36	14	4.0	3.6	7.9	9.6	9.4	34.5	40.0	25.5	7.27	56.0
5	Ckg	47	7									7.39	11.5

1. Gravel=75-2 mm
2. VCS=2-1 mm, CS=1-0.5 mm, MS=0.5-0.25 mm, FS=0.25-0.1 mm, VFS=0.1-0.05 mm, TS=2-0.05 mm
3. Silt=50-2 μm
4. Clay=<2μm
5. pH on saturated paste

TABLE 3. CHEMICAL ANALYSIS OF RHYOLITE SOIL IN THE CENTRAL DESERT OF BAJA

S. #	Horizon	Depth (cm)	Organic Carbon[1] g kg^{-1}	$CaCo_3$ equiv[2]. %	pH[3]	Extractable cations[4] Ca	Mg	Na	K	CEC[5]
						cmol$_c$Kg^{-1}				
1	A1	0-2	2.2	2.2	7.79	22.80	2.27	0.87	1.08	26.98
2	ABtk	2-8	0.8	2.7	7.82	27.59	2.02	1.71	0.95	27.92
3	Btk1	8-18	2.4	4.2	7.50	30.80	1.49	3.45	0.67	29.29
4	Btk2	18-32	1.1	5.5	7.63	24.75	1.66	10.92	0.63	30.61
5	Ck	32-36	0	56.0	7.27	26.86	1.07	8.06	0.14	12.18
6	Ckg	47	1.6	11.5	7.39	24.84	9.39	12.92	0.50	22.61

1. Organic carbon = (total carbon by combustion at 900°C).
2. Manometer method.
3. Saturated paste.
4. Extracted with 1.0 M NH_4OAC at pH 7.0.
5. Samples saturated with NaOAC at pH 8.2, washed with 95% ethanol, and extracted 1.0 M NH_4OAC to remote absorbed Na.

Soil material from the Al, Btk2, and Ckg horizons was sampled. Samples were sieved to remove the >2 mm fraction. Pretreatments included removal of carbonates using pH 5.0 NaOAC; removal of organic matter with pH 9.5 NaOAC. The soil from each horizon was dispersed and separated into its respective sand, silt and clay fractions using centrifugation and sedimentation methods. Magnesium and potassium-saturated clay samples were obtained by washing with M_gC1_2 or KCl, respectively. Na-saturated clay samples were obtained by washing with NaCl and dialysing to remove chloride, and were then freeze-dried.

Soil samples prepared for the study were subjected to the following analyse which are summarized as under:

1. X-ray Diffraction: X-ray diffraction (XRD) was performed using a Siemens D500 X-ray diffractometer, linked to a Daco MP microcomputer under a Siemens diffrac 11 software system, in a PDP 1123 computer.

   Three different types of samples, i.e. (001) oriented paste mounts, oriented slurries, and a side-packed powder mount, were analyzed. These samples represent the soils.

   Detailed methods of analysis and interpretation are discussed by Whitting and Allardice (1986).

2. Electron Microscopy: Transmission electron microscopy (TEM) was conducted using a Hitachi H-600 TEM operated at 75 KV. Analysis was made of a dilute 10:1 suspension made from the Na-saturated clay for the Al and Ckg horizons.

3. Thermogravimetric Analysis: Thermogravimetric analysis (TGA) was performed using a Dupont 951 Thermogravimetric Analyzer linked to a Model 9900 Computer/Thermal Analyzer. Analysis was made on the Na-saturated clay samples from each of the three horizons. Methods of analysis are discussed by Tan et al. (1986).

4. Infrared Spectrometry: Infrared analysis was conducted using a Mattson Cygnus 100 FTIR. A Na-saturated clay sample from the Ckg horizon was analyzed using the KBr pellet method (White and Roth, 1986).

RESULTS AND DISCUSSION

Identification

X-ray Diffraction: Because of the fibrous nature of palygorskite, oriented aggregates enhancing the (001) plane is evidently not feasible. Also, the degree of structural order in palygorskite is variable. The diagnostic peaks for palygorskite were:

10.4° A	(011)	most intense
6.4° A	(200)	
4.5° A	(040)	
4.3° A	(121)	
3.7° A	(221)	

Heating the sample at 350°C decreases the intensity of the main diffraction peaks and generates new maxima at 9.2 and 4.7°A. The main 10.4°A peak disappears completely between 600 - 800 °C (Figs. 1 - 4). These diagnostic peaks which upon heating showed changes are evident in the Ckg horizon; however, in the Al and Btk2 horizons the new maxima do not appear upon heating and the 10.4°A peak appears broader and much less intense than in the Ckg horizon. On heating, the 10.4°A peak in the upper two horizons actually becomes more intense. These data indicate that palygorskite concentration and degree of structural order increases in the lower horizon, relative to the Al and Btk2 horizons, where its presence is masked by the greater percentage of mica in the soil. In fact, our initial interpretation of the X-ray data suggested the presence of poorly crystalline mica.

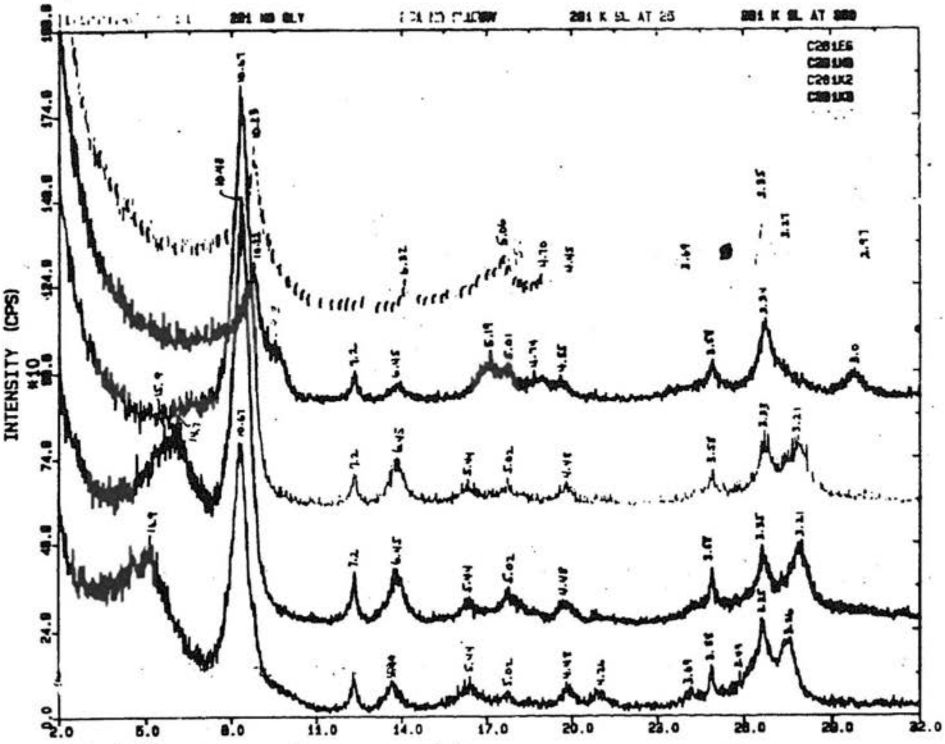

Fig. 1. X-ray diffractogram of parent material

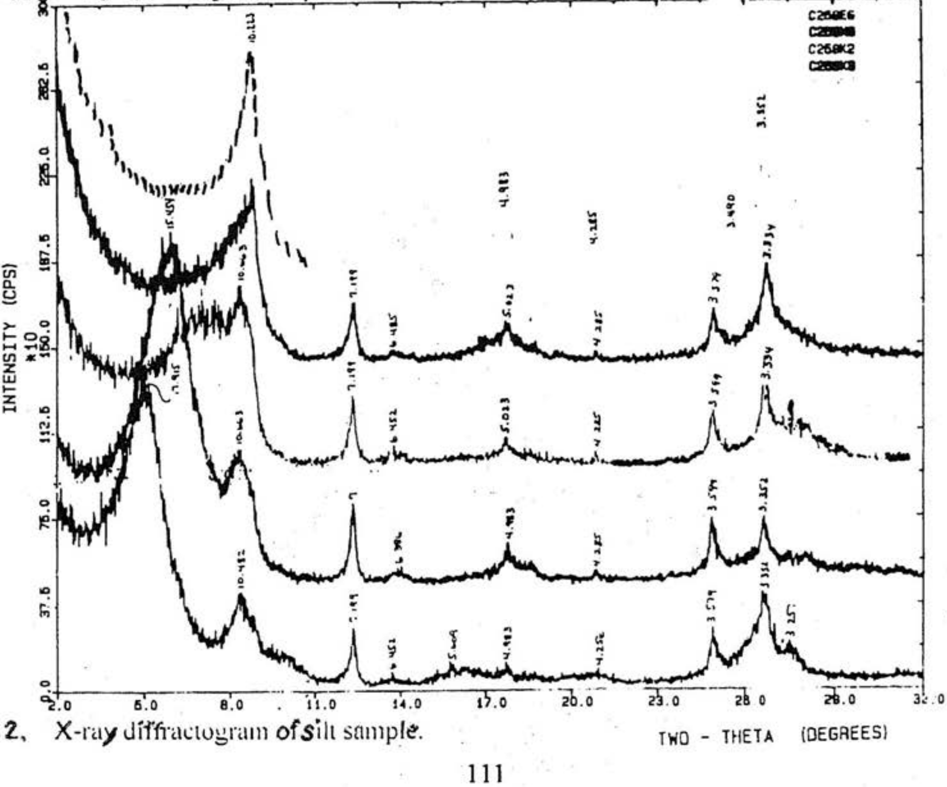

Fig. 2, X-ray diffractogram of silt sample.

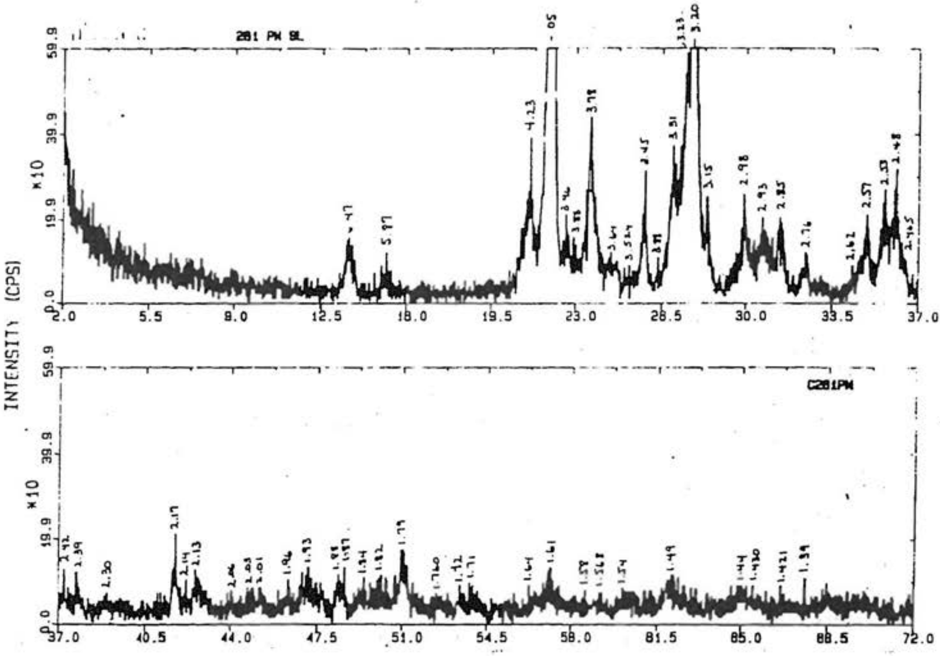

Fig. 3. X-ray diffractogram of clay sample.

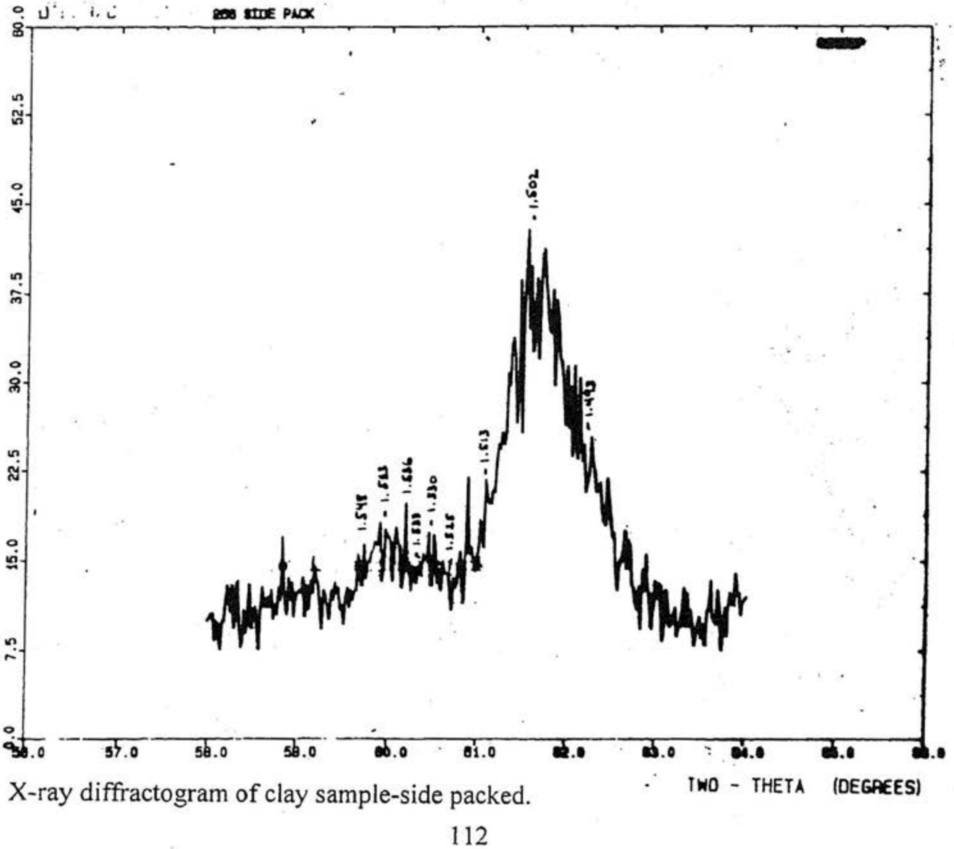

Fig.4. X-ray diffractogram of clay sample-side packed.

X-ray diffraction data for the medium silt fractions of each of the three horizons also indicated the presence of palygorskite.

TEM: TEM of the Na-saturated clay for the Al and Ckg horizons revealed, unusual acicular particles, which increased in concentration with depth. These particles were morphologically identical to palygorskite. At this point, X-ray diffraction data were reassessed and presence of palygorskite was confirmed. Figure 5 shows photograph taken of palygorskite in the Ckg horizon.

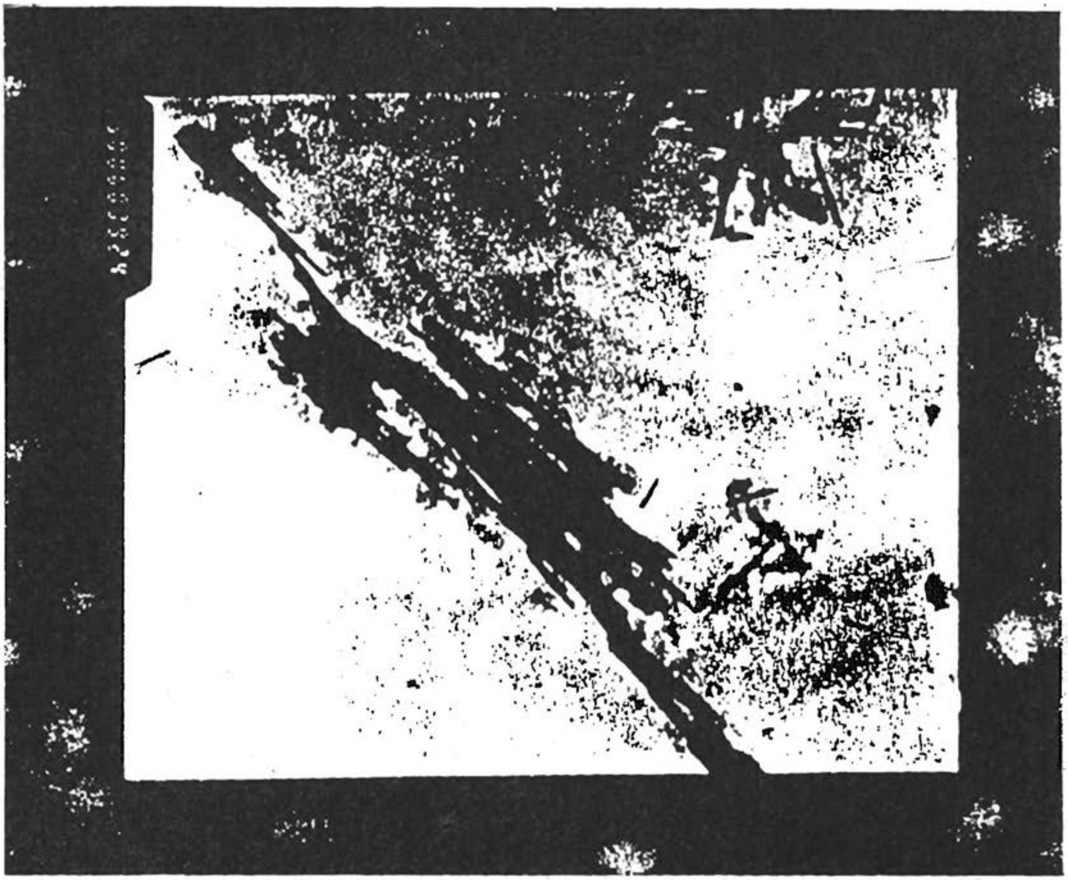

Fig. 5. TEM photograph of Palygorskite in Ckg horizon. (Fiber are 0.65 μ long).

Thermoqravimetric Analysis: Data generated corroborated previous findings using X-ray diffraction and electron microscopy. Typical palygorskite weight losses were shown, especially in the Ckg horizon, which correspond to 1) loss of adsorbed water, 2) loss of zeolitic water and part of the crystal lattice water, 3) further loss of crystal lattice water and dehydroxylation. Weight losses occurred at lower temperatures in the Btk2 horizon and the percent loss of zeolitic ater was less, indicating decreasing palygorskite crystallinity and lower concentration. In the Al horizon, an erroneous weight gain was seen, but generally the weight loss pattern suggests overlapping of different soil components, namely, kaolinite and montmorillonite. TGA plots are shown in Figs. 6-7.

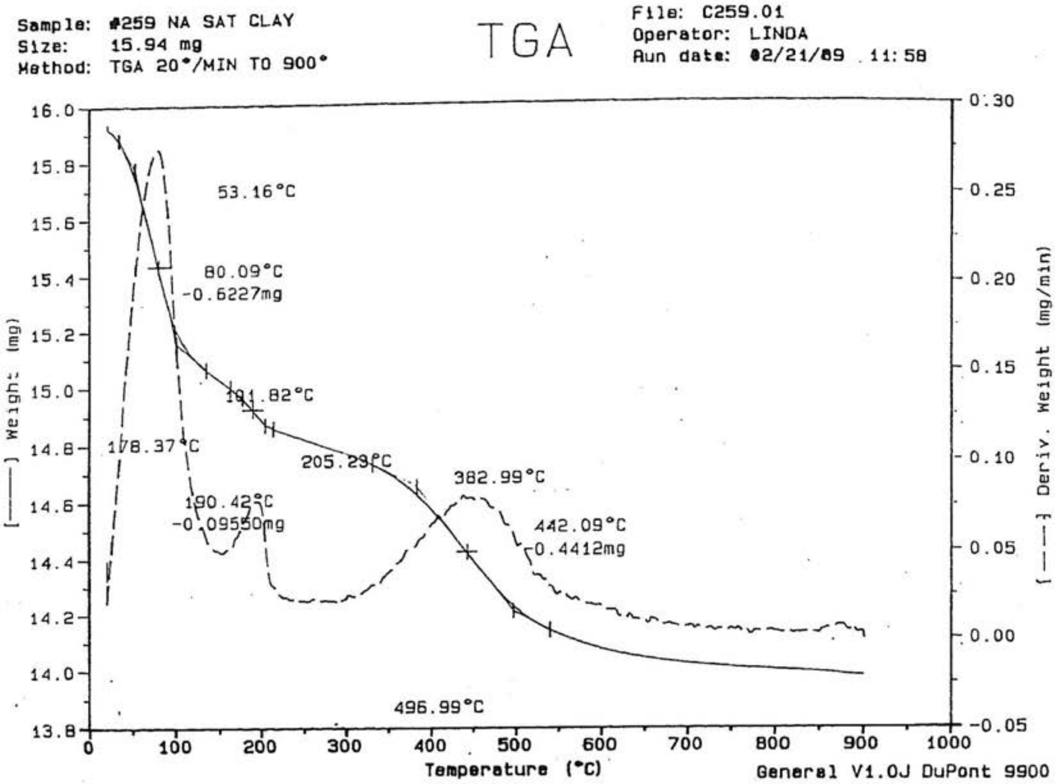

Fig. 6. Thermal analysis of Na saturated clay sample.

Infrared Spectroscopy: Once again, data obtained through FTIR corroborated previously generated data by other methods. The Na-saturated clay sample from the Ckg horizon displayed very similar absorbance bands compared with the attapulgite reference. Diagnostic absorbance bands corresponding to the following wavenumbers are present which are presented in Fig. 8.

3620	Structural OH stretching, originating in the aluminous octahedral layer.
930	Indicates dioctahedral character, A1A1OH deformation.
1180	Unique nature of 2:1 palygorskite ribbon layers.
1000	Shows complex Si-O stretching. 1180 band originates in straight Si-O-Si bonds linking ribbons together.
3580	Stretching and bending of water molecules.
3530	Originating in bound molecular water to octahedral.1660 cations.
3415	Originate with channel zeolitic 3290 water.

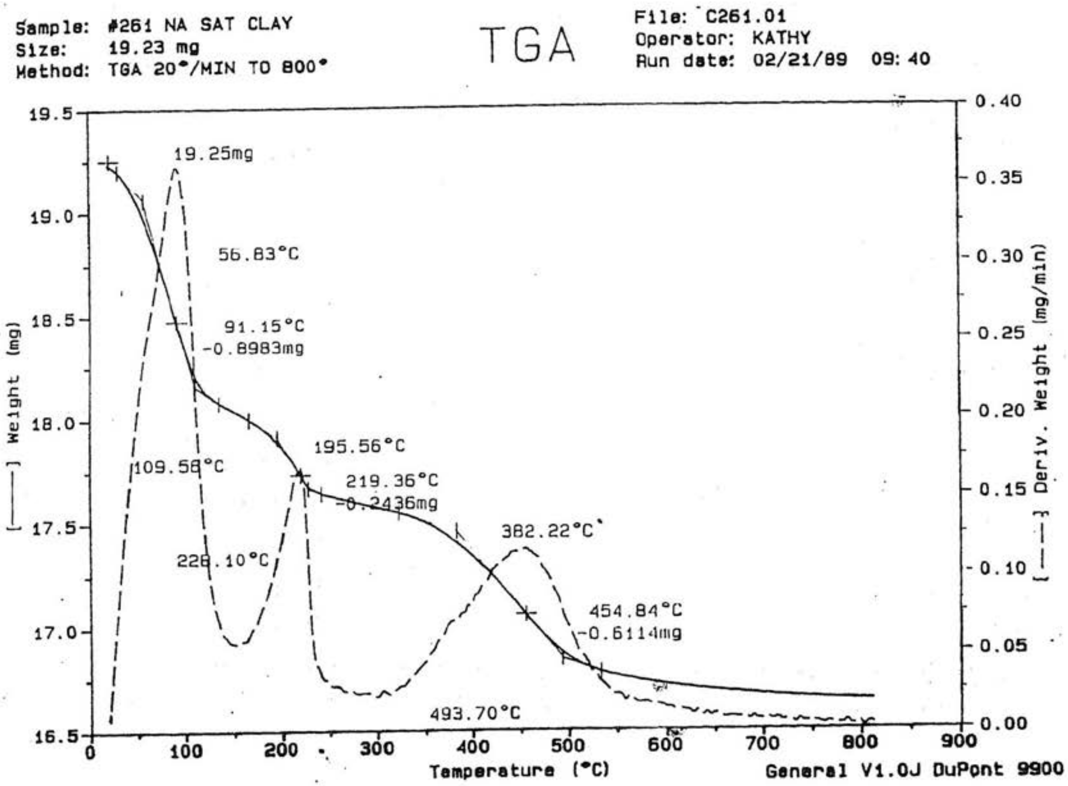

Fig. 7. Thermal analysis of 2nd Na saturated clay sample.

Distribution

Palygorskite is present in the clay and medium silt fractions, as evidenced by XRD data. The coarse silt fraction showed presence of small particles under the petrographic microscope, which might have been palygorskite, but the small size precluded positive identification. In a thin section of a clod in the Ckg horizon, masses of needle-like particles were seen in the voids; these may have been palygorskite, but further testing is needed to verify its presence.

The reported size of palygorskite (length =.2-2 μm) suggests that it will be most prevalent in the coarse clay fraction (.2-2 μm).

CONCLUSIONS

1. Palygorskite is present in the clay and medium silt fractions of each horizon. It is also present in the fine silt fraction.

2. Concentration and the degree of crystallinity of palygorskite increases with increasing depth through the soil profile.

3. X-ray diffraction should be run in conjunction with other diagnostic analyses to obtain accurate identification of soil components.

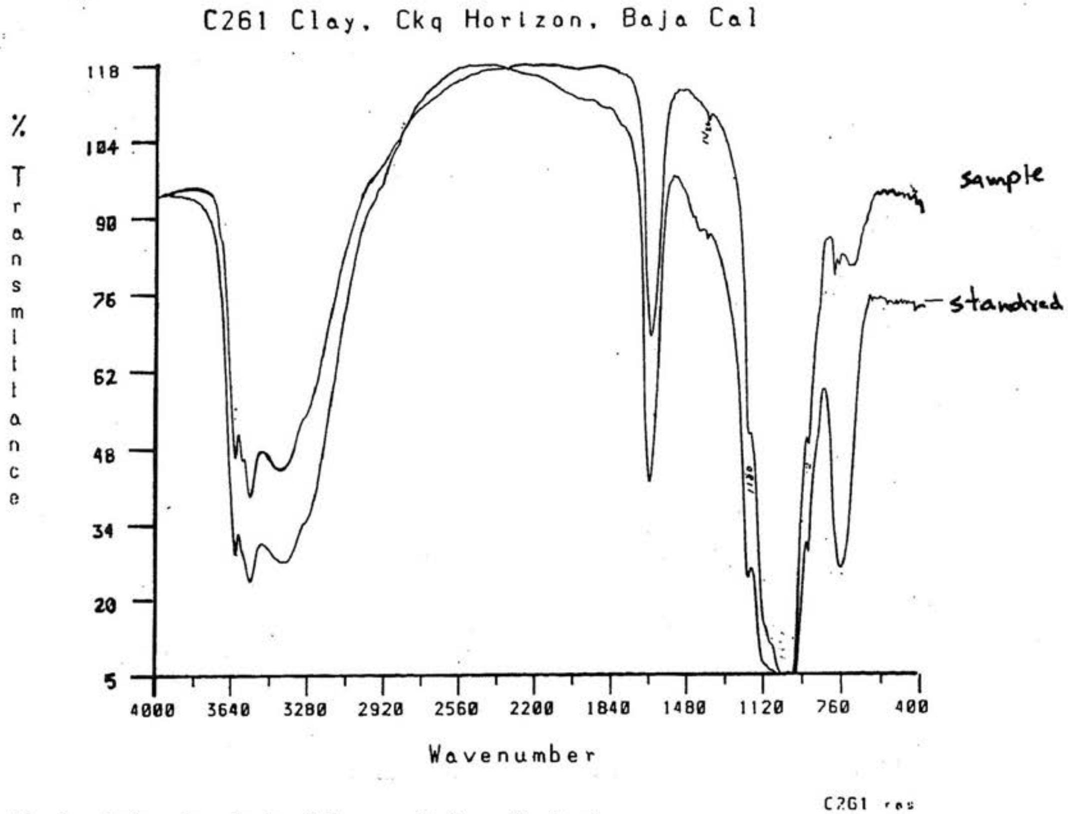

Fig. 8. Infrared analysis of clay sample from Ckg horizon.

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